

Quantum confinement observed in α -Fe₂O₃ nanorod-array

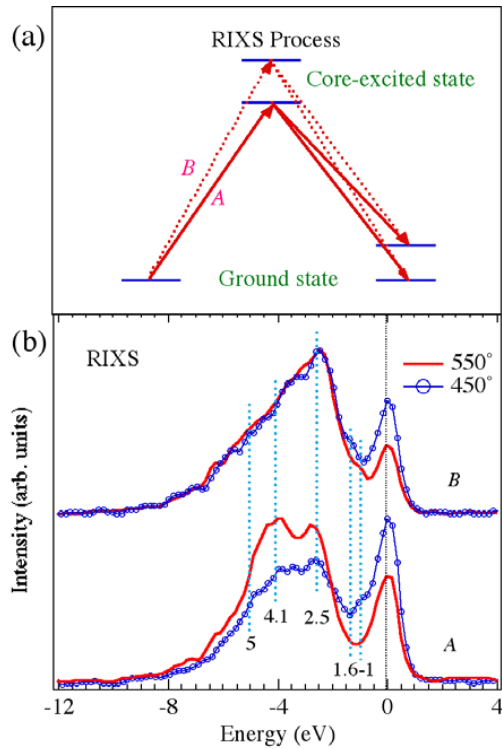
J.-H. Guo¹, L. Vayssieres², C. S  the², S. M. Butorin², and J. Nordgren²

¹Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

²Department of Physics, Uppsala University, Box 530, S-75121 Uppsala, Sweden

Resonant inelastic x-ray scattering (RIXS) has been applied to the studies of *dd* excitations in MnO and SrCuO₂Cl₂ [1,2]. The lowest-lying electronic excitations can be studied most directly by charge neutral spectroscopies, such as electron energy-loss spectroscopy (EELS) and optical absorption. The *dd* excitations in transition metal compounds are dipole forbidden and therefore very faint in optical spectroscopy.

α -Fe₂O₃ is an antiferromagnetic charge transfer insulator with a bandgap of 2.1 eV. Hematite crystallises in the trigonal system, rhombohedral R-3c group. The crystal structure is the corundum type (Al₂O₃) and can be described as a hexagonal close packed layering of oxygen with 6-fold co-ordinated iron ions yielding to face and edge-sharing octahedra. In an octahedral symmetry, a d⁵-configuration is found to have well-separated *dd*-excitations. Optical absorption spectroscopy of α -Fe₂O₃ has revealed many transitions ranging from infrared to ultraviolet.



Using the RIXS process, we probed specifically the *dd* excitations in α -Fe₂O₃ by transition sequence $2p^63d^5 \rightarrow 2p^53d^6 \rightarrow 2p^63d^5$. These *dd* transitions become fully allowed, and their intensity can be more easily calculated than that in optical spectroscopy and EELS.

The experiments were performed at beamline 7.0.1 [5] at Advanced Light Source, Lawrence Berkeley National Laboratory. The photon energy resolution was set to 0.2 eV for x-ray absorption spectroscopy (XAS) measurement. The resonant x-ray Raman scattering was measured using a grazing-incidence grating spectrometer [6]. The resolution of both monochromator and fluorescence spectrometer in RIXS measurement was set to 0.5 eV.

The measurements were done on synthetic α -Fe₂O₃ nanorods grown by Controlled Aqueous Chemical Growth [7]. The samples investigated in this letter are thin films, which consist of 3D crystalline array of hematite nanorods bundles of 50 nm in diameter and 500 nm in length perpendicularly oriented onto the substrate. Each bundle was found to consist of self-assembled nanorod of 3-5 nm in diameter. The samples were prepared by

heteronucleation growth and thermodynamic stabilization of akaganeite (β -FeOOH) in solution at 90°C onto the substrate and subsequently heated in air to 550°C to allow the crystal phase transition to hematite (α -Fe₂O₃) as confirmed by XRD.

In the resonant inelastic x-ray scattering process, final states probed via such a channel, which are related to eigenvalues of the ground state Hamiltonian. The core-hole lifetime is not a limit on the resolution in this spectroscopy [2]. According to the many-body picture, an energy of a photon, scattered on a certain low-energy excitation, should change by the same amount as a change in an excitation energy of the incident beam (see the decay route of core-excitation *B* versus that of *A* in Fig. 1a). Thus, the RIXS features have constant energy losses and follow the elastic peak.

The RIXS spectra at the Fe *L*-edge of α -Fe₂O₃ nanorods were recorded and shown in Fig.1. A few energy-loss features are clearly resolved. The low energy excitations, such as the strong dd and charge-transfer excitations, are identified in the region from 1 to 5 eV. The 1-eV and 1.6-eV energy-loss features originate from multiple excitation transitions. The 2.5-eV excitation corresponds to the bandgap transition, which is significantly larger than the 2.1-eV-bandgap of single-crystal hematite.

References:

1. S. M. Butorin, J.-H. Guo, M. Magnuson, P. Kuiper, and J. Nordgren, Phys. Rev. B **54**, 4405 (1996).
2. P. Kuiper, J.-H. Guo, C. S  the, L.-C. Duda, J. Nordgren, J. J. M. Poethuizen, F. M. F. de Groot, and G. A. Sawatzky, Phys. Rev. Lett. **80**, 5204 (1998).
3. L. A. Marusak, R. Messier, and W. B. White, J. Phys. Chem. Solids **41**, 981 (1980).
4. L.-C. Duda, J. Nordgren, G. Dr  ger, S. Bocharov, Th. Kirchner, J. Electr. Spectros. and Related Phenom. **110-111**, 275 (2000).
5. T. Warwick, P. Heimann, D. Mossessian, W. McKinney and H. Padmore, Rev. Sci. Instrum. **66**, 2037 (1995).
6. J. Nordgren, G. Bray, S. Cramm, R. Nyholm, J. E. Rubensson, and N. Wassdahl, Rev. Sci. Instr. **60**, 1690 (1989).
7. L. Vayssieres, H. Beermann, S.-E. Lindquist, and A. Hagfeldt, Chem. Mater. (in press, 2000).

This work was supported by the Swedish Natural Science Research Council (NFR), Council for Engineering Sciences (TFR), and the G  ran Gustafsson Foundation for Research in Natural Science and Medicine (GGS). Department of Energy Materials Sciences Division Contract DE-AC03-76SF00098.

Principal investigator: Jinghua Guo, Advanced Light Source, LBNL. E-mail: jguo@lbl.gov. Telephone: 510-495-2230.